

The Use of Field Deployable Instrumentation for the Monitoring of Munitions Constituents in Groundwater

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Introduction

- Long Term Monitoring of Groundwater
 - ▶ Can be required for 30+ years
 - Long after activities at a site have ceased
 - ▶ Regulatory approved methods/detection limits
 - ▶ Laborious and expensive process
 - Sample collection, overnight shipment under COC
 - ▷ Over \$160/cooler shipping costs alone
 - Fixed laboratory analysis can be slow and expensive
 - ▷ 30-60 days, \$225/sample for explosives
- Field analysis goals
 - ▶ Rapid (near real time)
 - ▶ Cheaper (no shipment costs)
 - ▶ Comparable results
 - Absolute detection, confirmation, and quantitation
 - ▶ NB, 1,3-DNB, 2,4-DNT, TNB, TNT, RDX
 - ▶ Demonstrated at 2 field sites, Louisiana and Milan AAPs



Deployable Mass Spectrometer

Field Extraction Equipment



ICx Griffin 400 and 450



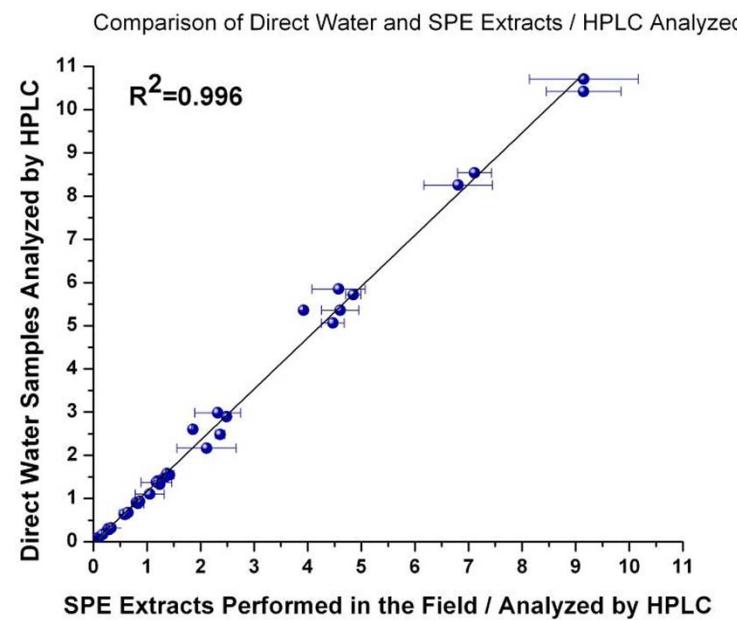
Field Portable = Minimal support services, i.e. power from a 5 kW generator, instrumentation fits in the same 4 m trailer the groundwater sampling supplies are transported in.

GC-MS is approximately 2' cube, weighs 35 kg



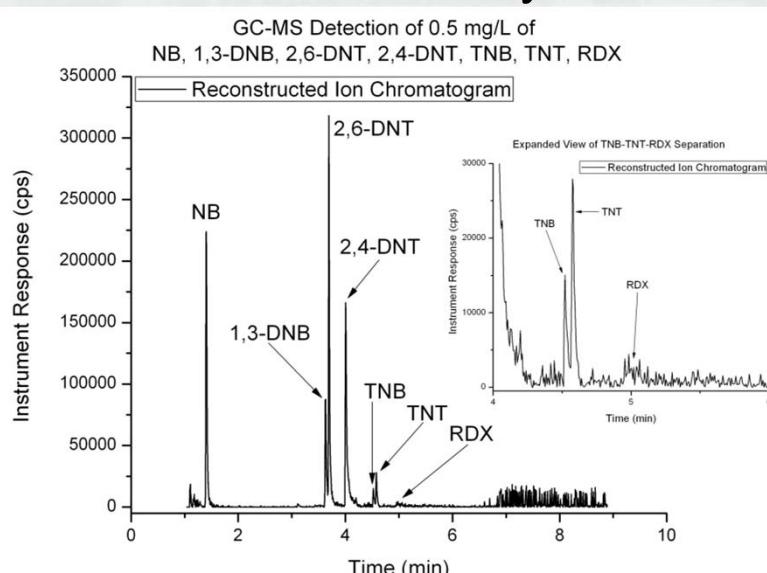
Field Extraction Methods

- Solid Phase Extraction Cartridges
 - ▶ Method 3535A
 - ▶ Compared to direct water analysis (values in ppm)
 - ▶ Same analytical method, HPLC, 8330B



Field Instrument Performance

- Instrument calibration range (SIM) 0.3 – 2.5 mg/L
 - Ground water concentration range 1.5 – 12.5 µg/L (CF of 200)
 - $R^2 > 0.95$ for all analytes
 - Quantitation limit 1 µg/L
 - Yields an effective analysis at 2 µg/L with SPE extraction concentration factor (~200x)
 - Time from analysis to data reporting is ~9 minutes



Analyte	MDL	0.001 ppm Verification	% REC
NB	0.0026	0.0012	120.0
1,3-DNB	0.0005	0.0011	110.9
2,4-DNT	0.0006	0.0008	75.8
TNB	0.0003	0.0005	52.2
TNT	0.0003	0.0013	133.2
RDX	0.0016	0.0012	117.0



Field Instrument LCS Recoveries

	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
DoD QSM Limits	50-140	45-160	60-135	65-140	50-145	50-160
LAAP Day 1	78	73	82	83	74	57
LAAP Day 2	58	47	60	73	59	33
LAAP Day 3	110	65	96	91	83	69
MAAP Day 1	100	98	91	81	82	55
MAAP Day 2	110	93	100	72	67	41
MAAP Day 3	99	100	110	62	70	57
MAAP Day 4	77	110	100	79	88	110

LCS spike concentration 10 µg/L



Field Instrument MS Recoveries

	NB	1,3-DNB	2,4-DNT	TNB	TNT	RDX
DoD QSM Limits	50-140	45-160	60-135	65-140	50-145	50-160
LAAP Day 1	96	86	91	74	63	45
	100	74	120	100	92	38
LAAP Day 2	92	180	170	7000	3600	-2200
	99	240	200	5300	2200	-3800
LAAP Day 3	80	72	73	75	72	54
	96	100	93	88	81	49
MAAP Day 1	120	110	110	66	55	9.8
	120	77	96	79	58	26
MAAP Day 2	110	68	100	59	54	260
	120	99	120	89	81	200
MAAP Day 3	160	110	110	22	61	20
	140	93	110	23	66	37
MAAP Day 4	70	99	94	66	86	33
	98	130	100	76	96	34



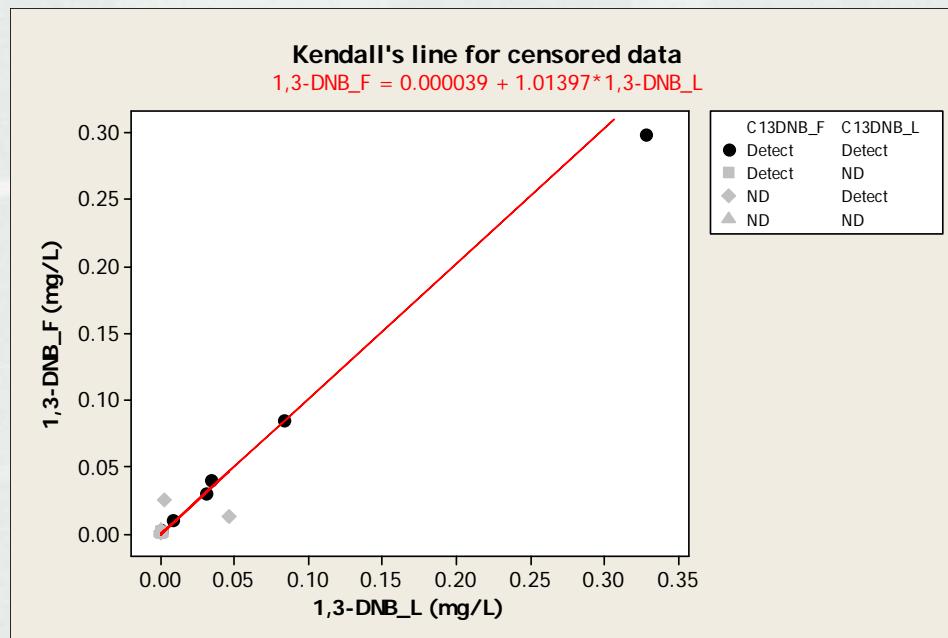
Laboratory-Field Comparison

- 28 groundwater samples collected from LAAP and MAAP
 - ▶ Additional 'synthetic groundwater' samples created by dilution of elevated samples with clean groundwater to make water samples with lower concentrations in a natural matrix
- Nitrobenzene (NB) was not detected in any groundwater sample by the field or laboratory methods
 - ▶ Limited comparison, but no false positives or negatives for the matrices tested



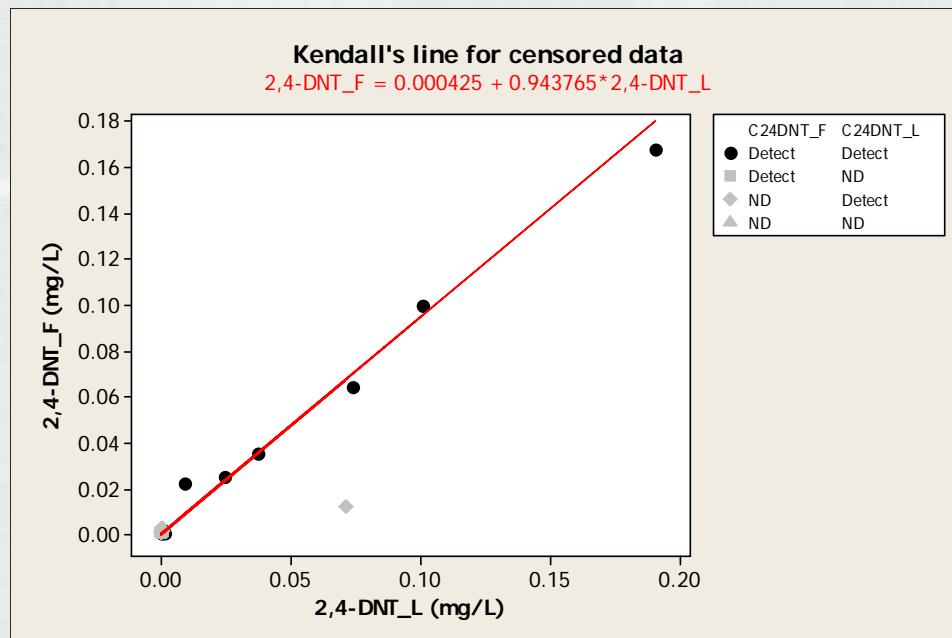
Laboratory-Field Comparison

- 1,3-DNB results show excellent agreement
 - ▶ Limited concentration range and dataset due to several non-detects
 - ▶ Ordinary least squares fit: $F = 0.86L + 0.018$
 - ▶ Kendall-Theil (K-T) Line: $F = 1.0 L + 0.00039$



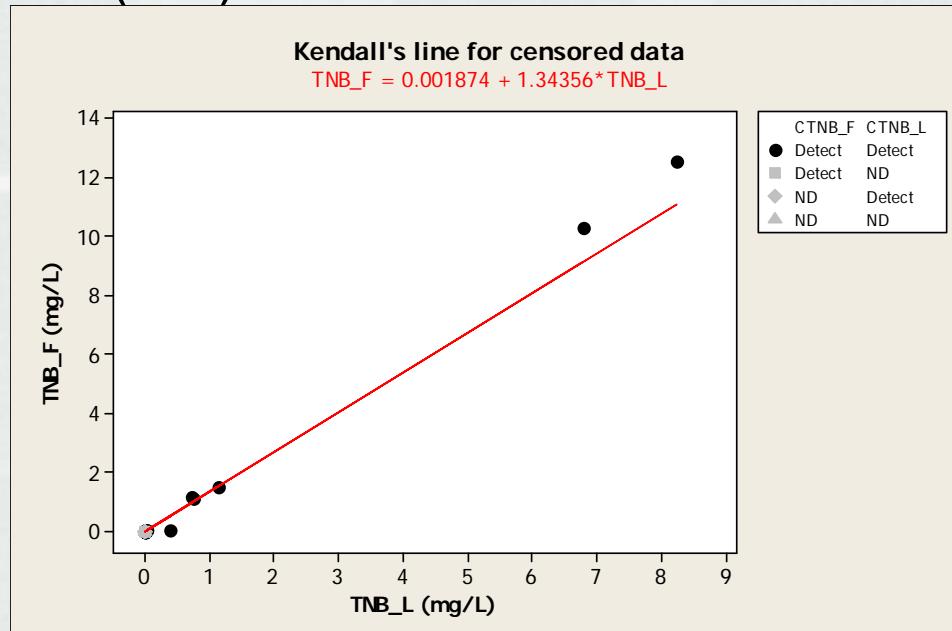
Laboratory-Field Comparison

- 2,4-DNT results show excellent agreement
 - ▶ Limited concentration range and dataset due to several non-detects
 - ▶ Ordinary least squares fit: $F = 0.88L + 0.0034$
 - ▶ Kendall-Theil (K-T) Line: $F = 0.94 L + 0.000042$



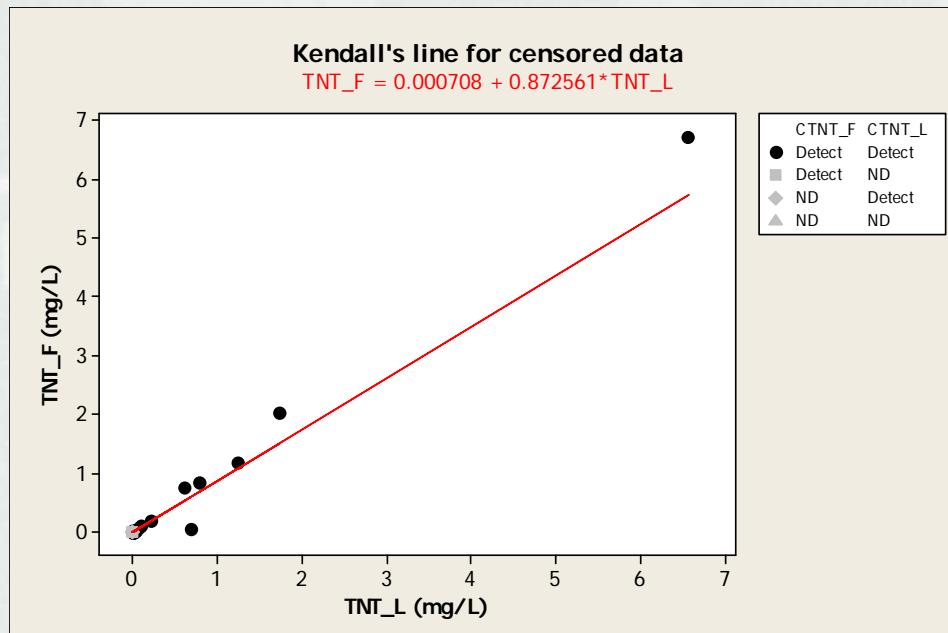
Laboratory-Field Comparison

- TNB results show positive bias
 - ▶ Possibly owing to TNT interference
 - (similar mass signatures and little chromatographic separation)
 - ▶ TNT was often an order of magnitude or more higher than TNB
 - ▶ Ordinary least squares fit: $F = 1.5L - 0.026$
 - ▶ Kendall-Theil (K-T) Line: $F = 1.3L + 0.0019$



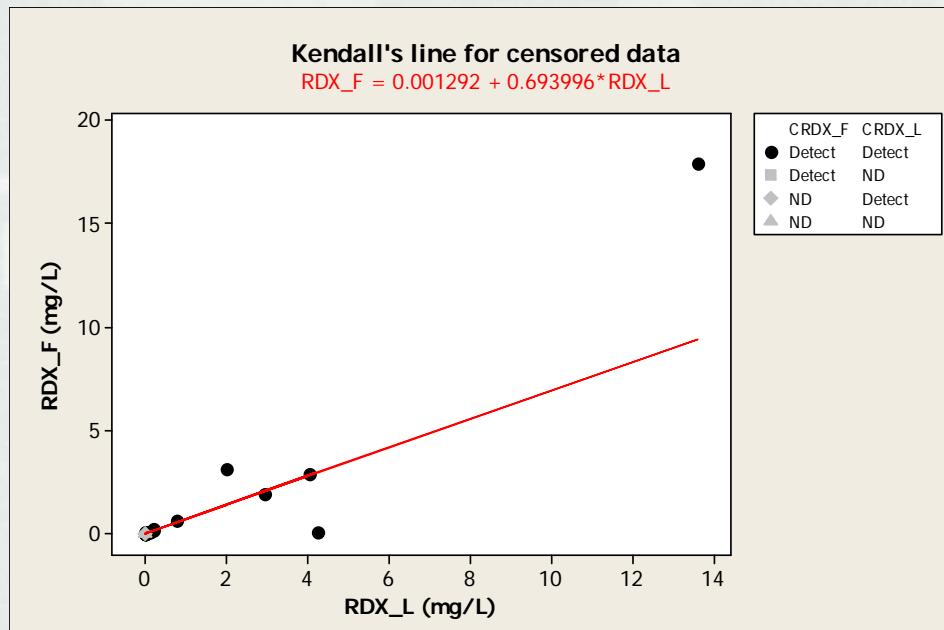
Laboratory-Field Comparison

- TNT results show excellent agreement
 - ▶ Screening level data below approximately 0.05 mg/L
 - ▶ Ordinary least squares fit: $F = 1.0L - 0.013$
 - ▶ Kendall-Theil (K-T) Line: $F = 0.87 L + 0.00071$



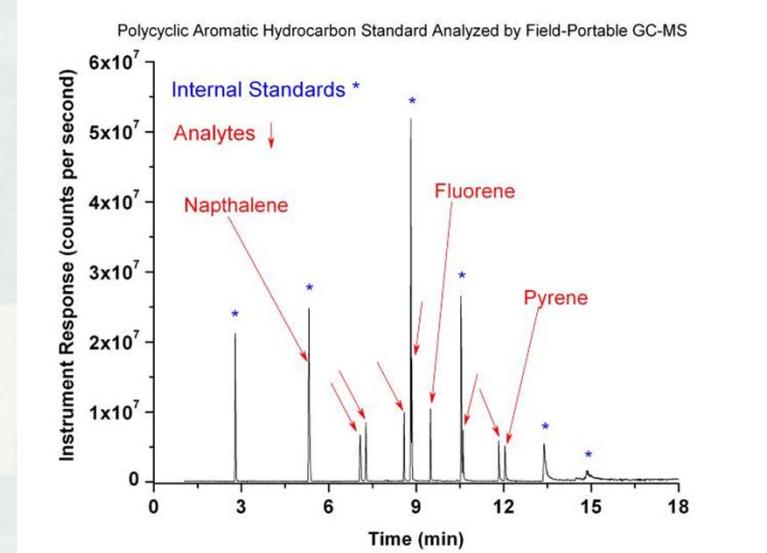
Laboratory-Field Comparison

- RDX results had significant scatter
 - ▶ Stability of RDX during thermal separation likely limits utility
 - GC-ECD by Method 8095 also has RDX/HMX issues
 - ▶ Screening level data by field GC-MS
 - ▶ Ordinary least squares fit: $F = 1.3L - 0.11$
 - ▶ Kendall-Theil (K-T) Line: $F = 0.69 L + 0.0013$



Other Applications

- PAH analysis in dredged material to identify oil spill residue during dredging
 - ▶ Deployed to Dredge BE Lindholm in August 2008
 - ▶ Analyzed water and sediment during operations
 - ▶ Near real time data lead to dredging decisions being made on scientific data rather than observations of 'sheen'



Conclusions

- Field portable instrumentation can provide near real time analysis of munitions constituents in water
 - ▶ Quantitative Agreement for Most Analytes
 - ▶ TNB was positively biased
 - Possibly due to elevated TNT
 - ▶ RDX is difficult by thermal separation methods
 - Limited to screening level data without further refinement
 - ▶ Method development and instrument optimization are critical



Future Work

- Delineation of PCB contamination at Anniston Superfund Site
 - ▶ Near real time analysis of sediments
- Other organic compounds
 - ▶ Pesticides, Gulf Oil Spill/PAH Analysis
- Further development of MIMS for direct analysis of water samples
 - ▶ No sample preparation/extraction needed



Funding

- ESTCP
 - ▶ ER-0922
- Environmental Quality and Installation Long Term Monitoring



Questions?

Thank You

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Laboratory-Field Cost Comparison

- Cost difference between the laboratory and field analysis
 - ▶ Breakeven point occurs at ~3.5 years
 - Assumes 12 5-day sampling trips/year and 25 samples analyzed per sampling trip. Total of 300 samples analyzed per year
 - ▶ Net present value (NPV) analysis
 - Savings of ~90K after 7 years (life expectancy of a field instrument)

